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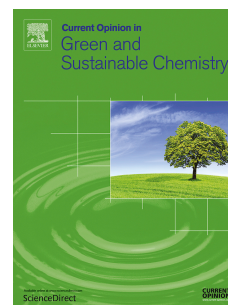
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Recent Advances on Carbon Dioxide Capture through a Hydrate-Based Gas Separation Process

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Abstract

Hydrate Based Gas Separation (HBGS) process is gaining interest globally as a greener solution for separation of CO₂ from gaseous streams. In this paper, recently published articles on the development of HBGS process as a technique for separation of CO₂ from flue gas, feed gas and high CO₂ natural gas streams are briefly reviewed.

Keywords: Hydrate Based Gas Separation; Gas or Clathrate Hydrate; CO₂ capture; Pre-combustion; Post-combustion

Introduction

Energy intensity of growing economy and carbon intensity associated with the energy system are two main factors that lead to excessive emission of CO₂ [1,2]. Conversely, CO₂ sinks are very limited [3]. Carbon Capture and Sequestration (CCS) initiatives are taken globally to dampen the impacts of CO₂ on the global climate. One of the strategies in CCS is to separate CO₂ from feed and flue gases. There are commercially available CO₂ capture technologies that are being used in various industrial applications absorption, adsorption, membrane separation and cryogenic distillation [4]. However, capturing vast amount of CO₂ by conventional technologies requires great amount of CAPEX and OPEX. For example, it was calculated that the deployment of absorption process to eliminate 16 mol% of CO₂ in flue gas, reduces 10% of thermal efficiency of a modern power plant. [4]. Therefore, minimization of energy requirements is one of the highest priorities for the future CCS technology development [5]. There are active and ongoing initiatives targeted to increase the energy efficiency and reduce the costs for the aforementioned technologies [6-14]. In addition, there are also rooms to develop novel and innovative technologies for CCS. Electrochemical pumps, chemical looping and hydrate-based gas separation (HBGS) are few examples of recent technologies being developed for separation of CO₂ [6, 10, 15].

Gas or clathrate hydrates are ice-like crystalline solids, in which small gas/liquid molecules are trapped inside cavities of hydrogen bonded water molecules. These solids are normally stable at moderate to high pressures from few kPa [16] to GPa [17] and low

temperatures from 140 K to 330 K [16]. Formation of gas hydrate is a thermodynamic-driven process. Recently, gas hydrate has been identified as a suitable medium for CO₂ capture, mostly from flue gas streams. [18-20]. Hydrate-based gas separation (HBGS) process is gaining popularity as a carbon capture technology due to its lower energy requirement and it is “greener”. [21]. In addition, the selectivity of CO₂ in this process is considerably high [16]. In this work, we attempt to present a brief review of recent studies on CO₂ capture via hydrate-based process.

Background

The separation of gases by hydrate formation was first introduced in 1940s when it was suggested for separation of argon from neon by utilization of SO₂ hydrates [22]. Only 60 years later, in 2000, the concept of separation of CO₂ from flue gas through hydrate formation was suggested through the analysis of CO₂ + N₂ hydrate phase diagram hydrate [23]. However, the operating pressure for such process is unfavorable as it could be as high as 83.5 bar at 275 K for a flue gas containing 17 mol% CO₂. To overcome the shortcoming, the inclusion of THF as a thermodynamic promoter to reduce the required pressure to 4.75 bar at 275K is suggested. It is shown that a two-step hydrate based separation process is feasible to recover 95 mol% of CO₂ from the studied flue gas [23]. In addition, Seo *et al.* measured phase boundaries of CO₂+N₂ and CO₂+CH₄ hydrate systems at various pressure and composition and their results indicated that separation of CO₂ from these mixtures is thermodynamically feasible. Moreover, they observed CO₂ uptake in the hydrate phase increased with the decrease in the system pressure, suggesting the operating pressure for such separation process should be set as low as possible [24]. Since then, a significant number of work on phase behavior measurement on CO₂+N₂ and CO₂+H₂ systems with or without promoters are published. Comprehensive reviews of these work until 2015 are available in Babu *et al.* [25], Dashti *et al.* [26], and Ma *et al.* [27]. In the following sections, the recent investigations on the development of HBGS process for CO₂ capture in the last 3 years are discussed.

Post-combustion CO₂ capture

In recent years, most of the research work related to HBGS are focused on separation of CO₂ from flue gas [28]. This scenario applies to existing conventional power plants or any other facilities dealing with production of energy by burning the fossil fuels. Typically, flue gas is predominantly N₂ with CO₂ concentration ranges from 15 to 20% while O₂ concentration ranges from 5–9%. Since the flue gas pressure is near atmospheric pressure, a compressor system is normally required to pressurize the gas [29, 30]. In addition, a cooling system is also needed to ensure the temperature of the system goes as low as 2 °C [31]. A typical schematic diagram for such a process is presented in Figure 1. The high pressure requirement for the system can be significantly reduced by utilization of thermodynamic promoters [25].

[INSERT FIGURE 1]

Figure 1. Simplified schematic diagram for post combustion HBGS technology for CO₂ capture

Prior to 2014, most of the reported data on HBGS process is related to batch process. However, Sun *et al.* has reported that continuous HBGS operation of CO₂-CH₄, CH₄-N₂ and CO₂-N₂ is possible by utilizing a new type of reactor and THF as the thermodynamic promoter [32]. They have reported that a recovery of more than 65% of CO₂ in CO₂-N₂ system is possible. More importantly, Sun *et al.* has successfully extended the HBGS study from elementary and exploratory investigation to a more practical condition.

Another important recent advancement in HBGS is the utilization of semi-clathrate hydrate to replace the conventional hydrate system. Kim *et al.* investigated CO₂ capture from flue gas by using the TBAC as the semi-clathrate promoter [33]. Their results indicated that semi-clathrate phase boundary shifted between 13 to 15°C compared to SI hydrate of CO₂+N₂ at the same pressure condition for a 20 mol% of CO₂ in gas mixture. In addition, they showed that the equilibrium temperature is increasing at constant pressure with the increase in CO₂ concentration of the mixture. This observation is extremely important and should be taken into consideration while designing a continuous HBGS process. During a continuous process, the gas phase concentration is changing in the crystallizer due to the enclathration of CO₂ and this will affect the degree of sub-cooling requirement for the system.

Apart for the usage of semi-clathrate for the development of HBGS process, a number of studies are focused on the utilization of new chemicals as hydrate promoters or mixed thermodynamic and kinetic promoters to reduce the pressure requirement for the system. One of the important studies is reported by Kumar *et al.* [34]. They studied the influence of mixed thermodynamic and kinetic hydrate promoter on the hydrate formation of a synthetic flue gas, consisted of $\text{CO}_2 + \text{N}_2 + \text{SO}_2$. Their results indicated that combining THF and SDS has positive impact on the total gas consumption during the process even though the amount of gas uptake is much lower than that of system with only SDS as promoter. Lee *et al.* investigated CO_2 separation from N_2 by changing the hydrate structure from sI to sH hydrate using neohexene as sH hydrate former [35]. Their results showed an improvement can be achieved for systems with concentration of CO_2 less than 20 mol%. However, increasing the CO_2 concentration leads to the same equilibrium condition regardless of the presence of neohexene due to the formation of sI hydrate as a more stable phase. Methylcyclopentane (MCP) is also studied as the structure sH promoter for CO_2 capture from flue gas with similar trend observed as of the neohexene systems [36]. Moreover, it was reported that the separation efficiency and gas uptake is reducing in the presence of MCP [36]. Lee *et al.* extended the idea of using sH hydrate for CO_2 sequestration [37]. They demonstrated by injecting flue gas into a sH crystalline network of methane + neohexene, CO_2 molecules replace CH_4 molecules in the crystalline structure and sequester while CH_4 molecules are recovered from the system [37].

Pre-Combustion

The pre-combustion CO_2 capture is mainly focused on integrated gasification combined cycle (IGCC). In this process, conventional fuels are converted into a syngas mixture consisted of H_2 (≈ 60 mol%) and CO_2 (≈ 40 mol%) with a small trace of H_2O , N_2 and CO . The gas stream is typically at pressure between 2.5 to 5.0 MPa and temperature of approximately 45°C [20]. A separation of CO_2 from the syngas must be performed before the syngas is fed to a gas turbine or a fuel cell [28]. Based on the pressure condition of gas stream, a HBGS process can be utilized to capture CO_2 directly from the syngas stream although a cooling system is still required to reduce the temperature of the stream.

Most of earlier studies on the CO₂ capture from shifted gas are focused on utilization of proper promoter to enhance the separation and moderate the operational condition of HBGS process. For pre-combustion applications, utilization of structure sII hydrate former, such as THF, propane and cyclopentane, is investigated. In addition, semi-clathrate hydrate formers such as TBAB, TBAF and TBANO₃ are frequently studied [25]. In a series of publication, Fukumoto *et al.* extended the semi-clathrate hydrate research by studying the tetra-n-butyl ammonium chloride (TBAC) and tetra-n-butyl phosphonium bromide (TBPB) systems for CO₂ hydrate, H₂ hydrate, and modeled the phase boundary of H₂ + CO₂ hydrate in the presence of tetra-n-alkylammonium/alkylphosphonium salt aqueous solutions [38-40]. Their findings indicate these salts enhance the separation between CO₂ and H₂ and their performance is concentration dependent.

A number of recent studies on pre-combustion HBGS process are focused on the type of reactor coupled with the usage of hydrate promoter. One of the most interesting is reported by Babu *et al.* [41]. Their experimental work showed that the presence of propane in the syngas mixture leads to an unusual behavior in the system where water molecules are migrating to the surface and form the hydrate on top of the silica sand. Based on this behavior, they proposed a semi-batch process for separation of CO₂ and H₂. In addition, Zheng *et al.* looked into the impact of a silica sand fixed-bed reactor properties on the kinetics of hydrate formation [42]. The studied properties are reactor orientation, bed temperature, bed volume and saturation. They found out the horizontal bed with higher surface area leads to faster hydrate formation. In addition, they reported water saturation is a critical parameter where low water saturation is preferred as this will give more space for gas to pass through the bed and eventually convert all available water to the hydrate. In addition, the usage of THF, TBAF, TBAB in fixed bed reactors made of silica gels or coal particles are reported although the results of those study are similar to previously reported by earlier studies [43-45].

Miscellaneous

In addition to pre- and post- combustion gas streams, there are few other studies targeting CO₂ separation from CO₂-CH₄ gas mixture to simulate shale gas mixture or natural gas with

high CO₂ concentration. The separation of CO₂ from a simulated shale gas mixture with 40 mol% of CO₂ is investigated with pure water, THF as hydrate promoter or TBPB as the semi-clathrate promoter [46, 47, 48]. Interestingly, the results indicate gas hydrates that are produced at lower driving force in pure water could potentially reach to the highest separation efficiency. Recently, Zhou *et al.* investigate the separation of CO₂ from CH₄ in a large-scale stirrer-tank reactor [49]. They mentioned that this process can be utilized for selective separation of CO₂ from CH₄. Unfortunately, when the CO₂ concentration increases in the feed gas, the separation efficiency decreases [49]. Partoon *et al.* introduced a new gas hydrate crystallizer in their attempt to utilize gas hydrate technology for separation of CO₂ from high CO₂ natural gas streams (60-80mol%) [50]. They studied the separation in a series of semi-batch process by using distilled water. Their results indicated that the process is not very feasible, as both gases are tend to form hydrate at experimental condition. Nonetheless, their experimental results showed that the formation rate of gas hydrate can be increased to more than 8 times higher than similar spray reactor, more than 10 times higher from stirrer reactors with SDS as kinetic promoter and more than 50 times higher than bubble reactors [51]. Nonetheless, due to the smaller amount of CH₄ in the gas mixture, they believed that capturing CH₄ can lead to better separation of these gases with the aid of sII hydrate former such as THF and acetone [52, 53].

Way forward

The recent studies on the HBGS process for CO₂ capture show that there is still long way to development of this process. The most challenging part of development is the scaling up of the process to continuous/semi-continuous setups. A proper reactor type and design for continuous production of gas hydrate is still a challenge. Once that is fixed, an economic evaluation can lead to a comprehensive comparison of HBGS process with other existing ones.

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